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From: R. E. Blanco

Chemical Technology Division
Laboratory Section

Report Period: 11/10/51-2/10/52

Problem No. TDSI-

Part

QUARTERLY REPORT

Title: RaLa Development

Work by: R. E. Blanco, D. M. Helton, A. H. Kibbey, J. F. Land, J. H. Pannell
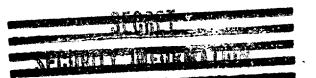
Secret Notebook No.1631, 1830

SUMMARY

Thirty kilocuries of Ba^{140} were processed in ORNL-RaLa run #46
with an overall loss of 8.6%, 0.6% from ion exchange and 8.0% from the pre-
cipitation steps. About 60% of the product was not soluble in water, how-
ever, after one fuming nitric acid precipitation but was completely soluble
after two precipitations. An investigation of the factors involved indi-
cated that the $Ba(NO_3)_2$ was probably not rendered insoluble as the result of
decomposition by radiation or heat but rather as a result of the presence
of sulfate or other resin radiation decomposition products. The fuming nitric
acid procedure was revised to ensure the complete removal of sulfate when the
mole ratio of $SO_4^=/Ba^{++}$ is one by means of one precipitation or complete
removal of sulfate for any mole ratio of $SO_4^=/Ba^{++}$ after two precipitations.
(See Table I.)

Preliminary results indicate that precipitation of lead-barium
nitrate from 13M nitric acid will eliminate the last traces of sulfate that
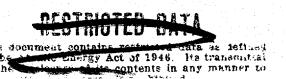
remain after the carbonate metathesis step. This precipitation would obviate the need for the pH adjustment on the highly radioactive Versene feed solution. The latter is now used to dissolve the water insoluble barium-lead sulfate residue.
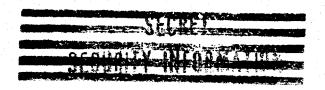
A process was developed for the recovery and purification of strontium from the ORNL-RaLa Versene waste solution. The yield for this process is > 97% and the product should contain less than <5.0 x 10^{-4}% and <0.1% of the Ce and Ba initially present in the feed solution (see flowsheet Figures 1, 2, and 3).

The total gross β activity processed in RaLa run #46 was approximately 40 kilocuries. The total β radiation received by the resin column was calculated as 0.515 KWH corresponding to 0.27 KWH/Kg over dry H^+ form resin. The titration of the column for capacity loss was erratic and indicated either a zero loss in capacity or a 20% increase in capacity. The latter would be possible as the result of the oxidation of C-C bands and the formation of carboxyl groups.

Scale demonstration runs of the over all MTR-RaLa process failed to achieve the necessary decontamination of aluminum and rare earths as shown in the previously published flowsheet. As a result, the sodium hydroxide elution of aluminum will be replaced with a sodium citrate elution at pH 3.2 which will selectively elute both aluminum and rare earths.

Spectrophotometric analyses of a sodium Versenate-sodium nitrate solution which had been irradiated by a Co^{60} source indicated that Versene is decomposed initially at a rate of approximately 0.69 milli moles/watt hour in an 8.40×10^{-4} watt/gm field and at 0.55 milli moles/watt hour in a 2.18×10^{-3} watt/gm field. These values are being rechecked to see if their

difference is due to rate of irradiation or to a possible difference in their equilibrium oxygen content. After twenty watt hours/gm of irradiation the concentration of Versene had decreased by about 50% and its rate of decomposition had apparently approached zero. Two mechanisms to describe this system are: (1) The organic radiation decomposition products are selectively oxidized in the later stages of irradiation and thus protect the Versene; or (2) The organic decomposition products absorb in the same spectrophotometric range as Versene and are thus mistaken for Versene. An exact analysis of the irradiated solutions will be attempted.

The pH of the Versene solutions (0.065M) rose from 6.3 at an approximate rate of 60 units/watt hour/gm to the range of 8.5 to 9.5 and then remained constant (see Figure 4.0).

1.0 ORNL-RaLa

RaLa run #46 processed 30,000 curies of barium with an overall loss of 0.6% from ion exchange and 8.0% from the precipitation steps. In general the process proceded very smoothly. Two difficulties were encountered, however, in that the samplers worked erratically during the pH adjustment period causing a delay and a consequent increase in column irradiation time of two hours. Also the product was not completely soluble in water after one fuming nitric precipitation. Development work designed to eliminate these difficulties is listed in the following sections.

1.1 Product Solubility

About 60% of the Ba product from the recent RaLa run was not soluble in water after one fuming nitric acid precipitation but was completely soluble after two precipitations. Three possible explanations for the formation of an insoluble salt from the solid $Ba(NO_3)_2$ precipitate are:

(1) Decomposition as a result of radiation (≈ 9.56 beta watt hrs./gm Ba $(NO_3)_2$);

(2) Thermal decomposition (86.6 calories)/gm of $Ba(NO_3)_2$; and

(3) presence of sulfate or other resin decomposition products.

Laboratory experiments showed, however, that baking a $Ba(NO_3)_2$ precipitate for ten minutes at $300^\circ C$ did not form an insoluble compound and irradiating solid $Ba(NO_3)_2$ for one week in the 3000 curie Co^{60} source (≈ 0.14 watt hour/gm $Ba(NO_3)_2$) did not form an insoluble compound. Experiments by Ghormley, in which $Ba(NO_3)_2$ was irradiated to 25 watt hours/gm of $Ba(NO_3)_2$ in a Van Der Graff beam or for eight days at the center of the X-10 pile, also showed no formation of insoluble material although 20.0 and 3.0% of the nitrates were converted to the nitrites in the two experiments respectively. It was concluded that the barium was insoluble due to the presence of sulfate.

Only 80% of the barium is precipitated as water soluble $Ba(NO_3)_2$ when the mole ratio of $SO_4^=/Ba^{++}$ is ~ 1.0 using the present flowsheet procedure for precipitation from 85% nitric acid. In this procedure the column product eluate, 16.0L of $9.0\underline{M}$ HNO_3, is evaporated to 2.0L and the barium precipitated by the addition of 6.0L of 91% HNO_3. Subsequent experiments showed, however, that a quantitative precipitation of $Ba(NO_3)_2$ was obtained when the column eluate was evaporated to 8.0L, and 9.0L of 91% HNO_3 added as precipitant. Two precipitations using this procedure would therefore produce pure $Ba(NO_3)_2$ from solutions containing any mole ratio of $SO_4^=/Ba^{++}$. This hypothesis was verified by a two cycle treatment of a solution containing a $SO_4^=/Ba^{++}$ mole ratio of 9.3 (see Table I).

The success of the above procedure is undoubtedly due to the fact that appreciable quantities of Ba SO_4 are not precipitated during the evapora-

tion to the larger volume due to the relatively high solubility of $BaSO_4$ in strong nitric acid, although partial precipitation of $Ba(NO_3)_2$ does occur during the evaporation. This theory is proved by the failure of 91% nitric acid to metathesize solid $Ba\ SO_4$. Treatment of $Ba\ SO_4$ with 91% nitric acid converted only 20% of the solid to water soluble $Ba(NO_3)_2$. Apparently only the outer part of each crystal is metathesized in this manner.

1.2 Conversion of Lead-Barium Sulfate to Nitrate with Nitric Acid

The metathesis of $Ba\ SO_4$ - $Pb\ SO_4$ to $Ba(CO_3)_2$ - $Pb\ CO_3$ with K_2CO_3 in the ORNL-RaLa process is not complete. As a result the barium is not completely soluble in the sodium acetate column feed solution and must be dissolved in Versene at pH 6.0-6.3. Elimination of the remaining sulfate would obviate the need for a pH adjustment on the highly radioactive feed solution.

Preliminary experiments on solutions containing 10% of the amount of sulfate originally present before carbonate metathesis indicated that the sulfate can be completely eliminated by dissolution of the $(Pb, Ba)(SO_4-CO_3)$ cake in nitric acid and precipitation of $Pb(NO_3)_2$ - $Ba(NO_3)_2$ from strong nitric acid. The procedure is to dissolve the cake in 15.0L of 6.0$\underline{M}$ HNO_3 and heat to 90-100°C for fifteen minutes to ensure the complete dissolution of the sulfates; cool, and add 15.0L of 90-92% nitric acid; filter, and dissolve the precipitate in the sodium acetate feed solution.

Several other aspects will be investigated before this procedure is recommended. They include the solubility of 120 gm of Pb and five gm of Ba in 6.0$\underline{M}$ nitric acid as a function of sulfate concentration; and the solubility of barium sulfate in nitric acid.
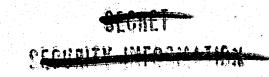
1.3 Radiation Stability of Dowex-50 Resin

During RaLa run #46 the resin column processed approximately 42,000 gross β curies, 30,000 of Ba^{140}, 1,250 of $Sr^{89,90}$, 700 of $Ce^{141,144}$, and 11,000 of La^{140}. All solutions passing into and leaving the column were analysed for these activities and their average residence time on the column calculated. The total β radiation energy received by the column was 0.515 KWH corresponding to 0.27 KWH/Kg over dry resin or 0.13 KWH/liter H^+ form resin. The column was titrated for total capacity both before and after the run. The first result indicated a gain in capacity of 20% which would indicate the formation of carboxyl groups from the oxidation of carbon linkages. A second titration as a recheck indicated zero change in capacity. It is unknown at present whether the first titration was in error or if carboxylic monomer decomposition products were washed from the resin between the first and second titrations. The resin will be titrated with a buffer solution after the next run in addition to the regular strong acid to determine the fraction of the capacity made up from carboxyl groups.

1.4 Production of Radiostrontium

A procedure was developed for the recovery and purification of strontium from the ORNL-RaLa Versene waste. The main steps in this process are listed as follows. A more detailed presentation was published in a separate memo (ORNL-CF-52-1-34).

(1) Adjust the Versene waste to pH 4.0-4.3 and pass the solution through a Dowex-50-Na^+ resin column. Barium and strontium are adsorbed while the bulk of the rare earths pass through.

(2) Selectively elute the balance of the rare earths with $0.5\underline{M}$ sodium citrate at pH 3.5.

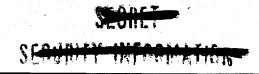(3) Selectively elute the strontium with 0.2$\underline{M}$ sodium citrate at pH 9.0.

(4) Elute barium with 0.25$\underline{M}$ Versene at pH 11.0.

(5) Clean and reactivate the column with nitric acid.

(6) Adjust the strontium citrate eluate to a pH of <1.0 and pass the solution through the column to readsorb the strontium and eliminate the citrate.

(7) Selectively elute the sodium with dilute hydrochloric acid.

(8) Elute the strontium in 9.0$\underline{M}$ nitric acid.

(9) A final purification is obtained by precipitation of strontium nitrate from 85% nitric acid.

See flowsheet (Figures 1, 2, and 3).

2.0 MTR-RaLa

2.1 Demonstration Runs

A flowsheet for the purification of barium by the MTR-RaLa process was issued in the last quarterly report as a summation of laboratory experiments performed on the various sections of the process. Subsequent scale runs on the overall process, containing the calculated amounts of fission products expected from a maximum irradiation of 37 days, failed to demonstrate the established decontaminations of aluminum and rare earths. It was found that the masses of aluminum and rare earths are additive during a fuming nitric acid precipitation. A large amount of aluminum reduces the solubility of the rare earths and vice versa. As a result the expected decontamination of cerium (rare earths) was not obtained during the first fuming nitric acid precipitation. It was also found that the sodium hydroxide used to selectively elute the aluminum from the resin column precipitated the rare earths

in the resin particles so that only ~50% of the rare earths were eluted by
the Versene solution.

2.2 Selective Elution of Aluminum and Cerium

The ion exchange process was reinvestigated for the purpose of eli-
minating the sodium hydroxide elution of aluminum and substituting an oxalic
and/or citric acid elution of both aluminum and rare earths.

A series of seven runs were carried out to study the variables
involved. The experiments showed that (1) sodium citrate at pH 3.0-3.5 is
much more effective than citrate or Versene at pH 6.0-7.0 for the selective
elution of aluminum and rare earths. Sodium citrate at pH 3.0 was the most
effective for elution of aluminum while pH 3.5 was the best for rare earth
elution. Citrate at pH 3.5, however, also complexes barium somewhat and
resulted in a 5% barium loss during the subsequent step for the selective
elution of strontium. Sodium citrate at pH 3.0-3.5 was also more efficient
for aluminum elution than oxalic acid at reagent pH 0.78. Sodium oxalate
at pH 2.5 eluted aluminum efficiently but precipitated the rare earths in
the resin particles and thus impaired their subsequent elution with citrate.

It was concluded that the optimum process condition for the selec-
tive elution of aluminum and rare earths is 0.5$\underline{M}$ sodium citrate at pH 3.2
and that this reagent should replace the sodium hydroxide in the present
flowsheet. Demonstration runs on the overall process are now underway.

2.3 Acid Hold Up in Celite Filter Cake

Demonstration runs showed that approximately two moles of nitric
acid were held up in the celite filter cake during the filtration of the
85% nitric acid from the first precipitation step. This amount of acid
corresponds to eighteen equivalents of acid/kilo of filter aid. The pre-

sence of this acid in the column feed caused the barium to be caught too low

on the column as the result of the complexing action of the nitrate, and

resulted in excess barium losses during subsequent elution steps.

In order to lower the acid hold up, the amount of celite filter

and was halved to a total of 40 gm, 20 gm as filter aid and 20 gms as the

filter precoat ($\approx$1 gm/in.^{2}). In addition the column feed was diluted to 20L

instead of 10L to decrease the effect of the nitrate.

Water will be used to dissolve the $Ba(NO_3)_2$ cake instead of sodium

nitrate in a further effort to lower the nitrate concentration. Since the

sodium ion is needed in the column feed to hold the resin in the sodium form,

about one half of the acid in the feed will be neutralized with sodium

hydroxide.

REB:bl

Table I

Conversion of Barium Sulfate to Barium Nitrate with Fuming Nitric Acid

Procedure:
(a) Dissolve the following in 16.0 liters of 9.0M HNO_3 at 90-100°C:
   0.0394 Moles (5 gm.) Ba^{++} plus Ba^{140} tracer.
   250 mg. Pb^{++} (For all runs except #10, which contained no Pb.)

1st Cycle:
(b) Evaporate to indicated residue volume and cool to 25°C.
(c) Add fuming nitric acid (90-92%).
(d) Filter and wash precipitate with 2.0 liters of 85% nitric acid.
(e) Dissolve precipitated barium nitrate in water.
(f) Dissolve precipitated barium sulfate in 16.0 liters of 9.0M HNO_3 at 90-100°C.

2nd Cycle:
(g) Evaporate (f) and repeat steps (b) through (f).

Run #	Mole Ratio SO_4/Ba	Residue Volume (Liters)	Fuming Nitric Acid (Liters)	Barium (Percent)			
				Filtrate	Water Soluble	Water Insoluble	Overall Material Balance
1st Cycle							
1	0.93	2.0	6	0.78	79.7	20.2	99.9
2	5.1	2.0	6	0.10	0.21	76.7	77.0
5	9.3	3.0	9	0.11	0.55	--	--
7	5.1	8.0	9	1.39	7.75	--	--
8	9.3	8.0	9	1.41	0.92	--	--
10	1.0	8.0	9	0.79	90.59	0.0	91.38
2nd Cycle							
5a	1.0	3.0	9	0.62	99.2	1.1	101.6
7a	1.0	8.0	9	0.64	82.82	0.56	93.16
8a	1.0	8.0	9	0.36	87.79	0.0	90.51

FIGURE I - PART I

FLOWSHEET: RECOVERY AND PURIFICATION OF
STRONTIUM FROM THE ORNL-RaLa VERSENE WASTE

D.G. 13494

VERSENE WASTE
1 Mole Versene
4 Moles NaOH
1.6 Moles HNO_3
50.0L
Evaporate to
14.0L

SODIUM VERSENATE
pH11, 0.25M
1.0L
1M NaOH
1.0L

TANK WASH
H_2O
6.0L

FEED ADSORPTION	RARE EARTH ELUTION	STRONTIUM ELUTION	BARIUM ELUTION	COLUMN CLEAN UP
Adjust pH to 4.0-4.3 20.0L	Sodium Citrate. PH3.5, 0.5M 10.0L	Sodium Citrate pH9.0, 0.2M 12.0L	Sodium Versenate pH11.0.25M 4.0L	2.0M HNO_3 3.0L 9.0M HNO_3 13.0L
WASH H_2O 2.0L	WASH H_2O 10.0L	WASH H_2O 2.0L	WASH H_2O 10.0L	WASH H_2O 10.0L

ION EXCHANGE COLUMN
3.1L. 15" in Height x 4" in Diameter
Dowex-50 Resin-Na^+, 60-100 Mesh

WASTE	WASTE	CRUDE PRODUCT	WASTE	WASTE
Ba <0.1% Sr <0.1% Ce ~98% 22.0L	Ba <0.01% Sr <0.01% Ce 1.5% 20.0L	Ba <0.05% Sr >99% Ce <0.5% 14.0L	Ba >99% Sr 0.1% Ce 0.5% 14.0L	Ba 0.5% Sr 0.02% Ce 0.06% 26.0L

TANK WASH
H_2O
5.0L

(See Part II)

FIGURE II - PART II

FLOWSHEET: RECOVERY AND PURIFICATION OF STRONTIUM FROM THE ORNL-RaLa VERSENE WASTE

70% HNO_3 0.6L

CRUDE PRODUCT

Sodium Citrate
pH < 1.0
19.6L

WASH
H_2O
10.0L

SODIUM ELUTION

1.0M HCl
10.0L

WASH
H_2O
10.0L

PRODUCT ELUTION

9.0 M HNO_3
16.0L

ION EXCHANGE COLUMN
3.1L, 15" in Height x 4" in Diameter
Dowex-50 Resin-H^+, 60-100 Mesh

WASTE

Ba   < 0.01%
Sr   < 0.01%
Ce   < 0.1%
Citrate
Nitrate
29.6L

WASTE

Ba   < 0.01%
Sr   < 0.01%
Ce   < 0.01%
Sodium
20.0L

COLUMN PRODUCT

Ba   < 0.1%
Sr   > 99%
Ce   < 0.01%
Na   < 1.5 gm
9.0M HNO_3

16.0L

(See Part III)

FIGURE III - PART III   DWG. #13506

FLOWSHEET: RECOVERY AND PURIFICATION OF
STRONTIUM FROM THE ORNL-RaLa VERSENE WASTE

Column Product

PRODUCT PRECIPITANT
91% HNO_3 3.0L
WASH
85% HNO_3 1.0L

PRODUCT DISSOLUTION
H_2O 0.5L

EVAPORATOR
Evaporate to 1.0L
85% HNO_3 4.0L

FILTER

WASTE	
Ba	<0.1%
Sr	1.0%
Ce	<0.01%
Na	<1.5 gm
Fe, Cr, Ni	
Organic Material	
5.0L	

PRODUCT	
Ba	<0.1%
Sr	>97%
Ce	~5x10-4%
Na	<20.0 mg
0.5L	

Figure 4.0

Irradiation Decomposition of Versene by Cobalt60

Solution: 0.065 M Sodium Versenate, pH 6.3; 0.10 M NaNO₃

Procedure: (A) Irradiate solutions with Co⁶⁰ source, at the indicated rates. Bubble water-saturated air through solutions continuously during irradiation.
(B) Sample and determine Versene concentration and pH.

Legend:
Irradiation Rate:
● 8.40 x 10⁻⁴ Watts/gm.
⊕ ○ 2.18 x 10⁻³ Watts/gm.
······ pH
——— Mm. Versene Destroyed